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THERMALLY CURABLE IMIDE CONTAINING MONOFUNCTIONAL POLYBENZOXAZINES

M. Sc. Thesis by
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Department : Chemistry

Programme : Chemistry

JUNE 2010

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Date of submission : 07 May 2010
Date of defence examination: 10 June 2010

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JUNE 2010

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

ISIYLA KÜRLEŞEBİLEN İMİT İÇEREN MONOFONKSİYONLU POLİBENZOKSAZİNLER

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Tezin Enstitüye Verildiği Tarih : 07 Mayıs 2010
Tezin Savunulduğu Tarih : 10 Haziran 2010

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HAZİRAN 2010

FOREWORD

I am very grateful to my supervisor Prof. Dr. Yusuf YAĞCI for his help and his deep interest in my research.
I would like to give my special thanks to Barış KIŞKAN for sharing his knowledge and his kind guidance during my master education.
I wish to express my special thanks to all the members of Yagci Lab for all their help, support and friendship. In particular, Muhammet Ü. Kahveci, Yasemin Yüksel Durmaz, Binnur Aydoğan, Mehmet Atilla Taşdelen, Kübra Demir, , Burçin Gacal, Demet Göen Çolak, Manolya Kukut, Alev Tüzün, Halime Cengiz, Serdar Okçu, Deniz Tunç, Elif L. Şahkulubey, Mustafa Uygun, Ali Görkem Yılmaz, Gökhan Açık, Çağatay Altınkök and Selim Beyazıt for all their help, kindness and support in all possible ways during my laboratory work.
I would like to thank to my best friend Zeynep Beyazkılıç for helping and guiding me with her kind patience everytime who has been a great source of motivation and inspiration.
Finally, This thesis is dedicated to my parents who have supported me all the way since the beginning of my life.

Thank all of you very much…

June 2010

Hande Çelebi
Chemist

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ABBREVIATIONS

PE	**:** Polyethylene
PP	**:** Polypropylene
PTFE	**:** Polytetrafluroethylene
PS	**:** Polystyrene
PVC	**:** Polyvinylchloride
PMMA	**:** Polymethylmethacrylate
KOH	**:** Possium hydroxide
'H-NMR	**:** Proton Nuclear Magnetic Resonance Spectroscopy
FT–IR	**:** Fourier Transform Infrared Resonance
DSC	**:** Differential Scanning Colorimetry
Tg	**:** Glass Transition Temperature
PBZ	**:** Polybenzoxazine
App	**:** Ring Opening Polymerization
RLi	**:** Alkyl - Lityum
MeOH	**:** Methanol
Mn	**:** The number average molecular weight

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THERMALLY CURABLE IMIDE CONTAINING MONOFUNCTIONAL POLIBENZOXAZINES

SUMMARY

Recently, high performance polymeric materials have received considerable studies for their wide application in electronics, biomaterials, and other industrials. Among the developed materials, polybenzoxazines possess outstanding properties of small shrinkage in curing, low water absorption, good thermal stability, and high glass transition temperatures. These advantages of benzoxazines receive considerable increase on the studies of benzoxazines and their corresponding polymers.

At the present there is considerable interest not only in synthesis of new types of plastic materials, but also in the modification of existing polymers in order to vary its properties to meet requirements for new applications.

In this study, firstly occured the imide derivatives, then formed imide containing benzoxazine monomers and finally converted to polybenzoxazines. Thus,the new material have thermal stability and non flammable property that is provided thermally curable and penetrable derivatives of benzoxazine.

Experimentally, Imide derivatives were synthesized with 4-aminophenol.This reaction is called as imidization. Monomers were syntesized by the reaction of 1,3,5-tribenzyl-1,3,5-triazinane. The spectral and thermal analysis confirmed the presence of benzoxazine functionality in the resulting polymers which are formed by thermal curing. These polymers are convenient to form structure that consist of benzoxazine units which create crosslinked network and impart the polybenzoxazine properties whereas the imide units form the non-flammable along the backbone. It is shown that imide containing benzoxazine undergoes thermal curing in the absence of any catalyst forming polybenzoxazine thermoset with high thermal stability. The structure of the end product is characterized by H-NMR, FT-IR, DSC, TGA.

ISIYLA KÜRLEŞEBİLEN İMİT İÇEREN MONOFONKSİYONLU POLİBENZOKSAZİNLER

ÖZET

Son zamanlarda yüksek performanslı polimerik malzemeler; elektronik, biyomalzeme ve diğer endüstriyel alanlardaki geniş kullanım yelpazelerinden dolayı bir çok önemli çalışmalara konu olmuştur. Benzoksazin polimerler, reçineleşme sırasındaki ufak hacim değişiklikleri (büzüşme), düşük miktarda su absorplamaları, ısısal dayanımları ve yüksek camsı geçiş sıcaklıkları gibi göze çarpan üstün özelliklere sahiptirler. Bu özellikler benzoksazin ve benzoksazin polimerleri hakkında yapılan çalışmaların önemli bir şekilde artmasına sebep olmuştur.

Günümüzde, sadece yeni tür plastik malzemelerin sentezlenmesi değil, aynı zamanda yeni uygulamaların getirdiği gereklilikleri karşılamak için varolan polimerlerin modifiye edilmesi ayrı bir önem kazanmaktadır.

Bu çalışmada, önce imit türevleri oluşturulmuştur. Daha sonra imit içeren benzoksazin monomerinin türevleri sentezlenmiştir ve son olarak polibenzoksazinlere dönüştürülmüştür. Böylece ısısal dayanıklı ve yanmayan ısıyla kürleşebilen benzoksazin polimeri elde edilmiştir.

Deneysel olarak imit türevleri 4-amino fenol varlığında sentezlenmiştir. Bu reaksiyon imitleşme reaksiyonu olarak anılır. Monomerlerde 1, 3, 5-tribenzil - 1, 3, 5-triazinan ve imit türevlerinin reaksiyonu ile sentezlenmiştir.

Oluşturulan polimerdeki benzoksazin fonksiyonel grubunun varlığı spektral ve termal analizlerle tespit edilmiştir. Elde edilen ürünün imit bölümü yapıya yanmazlık özelliği katarken benzoksazinin termal olarak çapraz bağlanabilme özelliği sayesinde termal olarak stabil bir yapı oluşumu gerçekleşir. İmit içeren polibenzokazinin termal olarak kürlenebildiği ve yüksek termal kararlılığa sahip olduğu gösterilmiştir. Yapı ^{1}H-NMR, FT-IR, DSC, TGA enstrümantal cihazları ile karakterize edilmiştir.

1. INTRODUCTION

In recent years, the performance requirements have risen for polymeric materials as their electronic and structural applications have gone through technological advances. One of the most promising material is benzoxazine polymers which is a new type of addition polymerized phenolic system, having a wide range of fascinating characteristics. It overcomes several shortcomings of conventional novolac and resole type phenolic resins. These include nearly zero shrinkage upon curing, thermal stability, chemical resistance and flame retarding properties along with the mechanical performance. Benzoxazine monomers can be simply synthesized from phenols, primary amines, and formaldehyde. Polybenzoxazines can be formed by thermally activated ring-opening of the benzoxazines without any catalysts, and no byproducts or volatiles are released. By using particular types of amine and phenol, polybenzoxazines with char yield as high %80 have recently been obtained. These advantages of benzoxazines receive considerable increase on the studies of benzoxazines and their corresponding polymers. Various research groups have been studied benzoxazine monomers and blends, their reaction mechanisms of polymerzation and behaviour of the cured materials with different synthetic strategies. But, pure polybenzoxazine based polymers also have disadvantages, in terms of (i)flammability, (ii) difficulty in processing and (iii) brittleness. To overcome this disadvantages, there are various strategies, such as (i) preparation of modified monomers with additional functionality, (ii) synthesis of novel polymeric precursors and (iii) by blending with a high performance polymer or filler and fibers. Polybenzoxazines prepared from the monomers precursor are associated with some limitations on their use in practical applications. The monomers are usually powder and processing into thin films is rather difficult. Addition of elastomeric materials to brittle resins is a well known approach to improve the ductility. But while improvement in ductility of benzoxazine may be achieved using this approach, it sacrifices the intrinsic advantages of thermosetting resins. In addition to this the formed polymers are not only brittle but also not suitable for high temperature applications. By this way further reinforcing of thermal properties is also expected.

One approach to reinforce the performance of polybenzoxazine is the modification of monomer. In the modification method, the introduction of thermally stable structure into the backbone of benzoxazine is considered. To properly address these issues and overcome the associated disadvantages, Polymers with imide moieties in the molecular backbone are considered as high performance polymers. They have unique temperature stability, high mechanical performance and excellent chemical resistance. By taking advantage of the molecular design flexibility, the benzoxazine monomers with imide moieties, namely the imide-benzoxazines were synthesized and the properties of their polybenzoxazines were investigated. The completely cured polymer exhibited good thermal stability and flame retardancy which is the aim of this work.

2. THEORETICAL PART

2.1 Polymerization

2.1.1 Chain-growth Polymerization

In chain-growth polymerization, propagation is caused by the direct reaction of a species bearing a suitably generated active center with a monomer molecule. The active center (a free radical, an anion, a cation, etc.) is generated chainwise by each act of growth; the monomer itself constitutes the feed (reactive solvent) and is progressively converted into the polymer. A chainwise polymerization proceeds exclusively by monomer + macromolecule reactions. When the propagation step is fast compared to the initiation step, long chains are already formed at the beginning of the reaction. The main parameters controlling the polymer structure are the functionalities of the monomers and the ratios between the initiation and propagation rates and between initiator and monomer concentrations.

2.1.2 Step-growth Polymerization

Step-growth polymerization proceeds via a step-by-step succession of elementary reactions between reactive sites, which are usually functional groups such as alcohol, acid, isocyanate, etc. This polymerization method typically produces polymers of lower molecular weight than chain reactions and requires higher temperatures to occur. Step-wise reactions involve two different types of di-functional monomers or end groups that react with one another, forming a chain. A step-growth polymerization (with or without elimination of low-molar-mass products) involves a series of monomer + monomer, monomer + oligomer, monomer or oligomer + macromolecule, and macromolecule + macromolecule reactions. The molar mass of the product grows gradually and the molar mass distribution becomes continuously wider. Functionalities of monomers and the molar ratio between coreactive sites are the main parameters for controlling the polymer structure.

2.2 Classification of polymers

2.2.1 Thermoplastics

The thermoplastics are often described as linear polymers. Strong covalent bonds exist along the chains (primary bonds) but the interatomic forces between the chains (secondary bonds) are weak that are build-up of long chains. Packing together of the long molecules in a great variety of configurations including amorphous (e.g. polystyrene), crystalline or more frequently partly crystalline or semicrystalline (e.g. polyethylene) structures. The thermoplastics can be melted and solidified repeatedly [1]. The melting temperature depends on length of chains and in practical cases is not so sharp as that in metals. The linear polymers are usually made by additional polymerization, meaning that one kind of unsaturated molecules is joined together by covalent bonding. Typical example is the formation of polyethylene from ethylene (CH_2=CH_2) as a monomer (2.1).

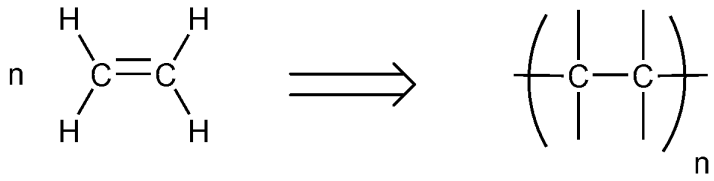


Figure 2.1 Polymerization of ethylene

In this case the group –[–CH_2-CH_2–] – is the constitutional unit, n is the number of monomers in the polymer (degree of polymerization). In polyethylene, n can be as large as 50,000 to 500,000. In Table 2.1, the composition and use of several thermoplastics are listed.

2.2.1 Thermosets

In thermosets or resins, network structure results in improved strength in which cross-linking agents rigidly bond the chains together by covalent bonds. These polymers can not be melted without degradation and are prepared usually by condensation polymerisation, reacting two components (a resin and a hardener) either at room temperature or on heating. In this case different kind of molecules is joined by a chemical reaction that releases a by-product, a small molecule such as

water [2]. The thermosets have generally amorphous structure. The prototype of network polymers has been the phenol-formaldehyde, one of the first synthetic polymers.It is well known under its trade name Bakelite.

Table 2.1 Composition and use of thermoplastics

Thermoplastic	Composition	Uses
Polyethylene, PE	Partly crystalline	Tubing, Film, Bottles, Cups, Electrical insulation, Packaging
Polypropylene, PP	Partly crystalline	Same uses as PE, but lighter, stiffer, more resistant to sunlight.
Polytetrafluroethylene, PTFE	Partly crystalline	Teflon, Good high-temperature polymer with very low friction and adhesion characteristics. Non-stick saucepans, bearing, seals.
Polystyrene, PS	Amorphous	Cheap mouldeal objects, Toughened with butadiene to make high-impact polystyrene (HIPS). Foamed with CO2 to make common packaging.
Polyvinylchloride, PVC	Amorphous	Architectural uses(window frames, etc.). Gramophone records. Plasticized to make artificial leather, hoses, clothing
Polymethylmethacrylate, PMMA	Amorphous	Perspex, Lucite, transparent sheet and mouldings. Aircraft windows, laminated windscreens.
Nylon 66	Partly crystalline when drawn.	Textiles, rope, mouldings.

Thermosetting polymers may be formed in two ways:

1. By polymerizing (step or chain mechanisms) monomers where at least one of them has a functionality higher than 2.

2. By chemically creating crosslinks between previously formed linear or branched macromolecules (crosslinking of primary chains, as vulcanization does for natural rubber)

Table 2.2 Composition and application of some thermoset

Thermoset	Composition	Uses
Epoxy	Amorphous	Fiberglass, Adhesives. Expensive
Polyester	Amorphous	Fiberglass, Laminates. Cheaper than epoxy.
Phenol-formaldehyde	Amorphous	Bakelite, Tufnol, Formica. Rather brittle.

2.2.2 Elastomers

The elastomers or rubbers are either natural or synthetic linear polymers that are somewhere between the linear and network polymers. They consist of linear chains but the chains are cross-linked in several places e.g. in rubber, sulphur atoms join the elastomer chains together [3].

The elasticity of rubber is determined by the number of cross-links. Low sulphur additions leave the rubber soft and flexible. Increasing the sulphur content of the rubber makes it more rigid

Table 2.3 Composition and use of elastomers

Elastomer	Uses	Composition
polyisoprene	Amorphous except at high strains	Natural rubber
polybutadiene	Amorphous except at high strains	Synthetic rubber
polychloroprene	Amorphous except at high strains	An oil-resistant rubber, used for seals.

2.3 Phenolic Resins

Phenolic resins include synthetic thermosetting resins such as obtained by the reaction of phenols with aldehydes which are formed by a step-growth polymerization reaction that can be either acid- or base-catalysed. Prominent features of phenolic resins are; excellent thermal behaviour, high strength level, long term thermal and mechanical stability, excellent fire, smoke and low toxicity characteristics, excellent cost performance characteristics.

There are two main types of phenolic resins:Resoles or one stage resins; the polymerization is carried out in the presence of an alkaline catalyst have a short shelf life. They are referred to as one step phenolics because they do not require curing agents, only heat. Novalacs or two stage resins; the polymerization is carried out in the presence of an acid catalyst such as oxalic acid, sulfuric acid, hydrochloric acid, formic acid.

2.4 Chemical Methodologies for Synthesis of Benzoxazine Monomers

Benzoxazine monomers are typically synthesized using phenol, formaldehyde and amine (aliphatic or aromatic) as starting materials either by employing solution method or solventless method. Using various types of phenols and amines, having different substitution groups attached, various derivatives of benzoxazine monomers can be synthesized. These substituting groups can provide additional polymerizable sites and also affect the curing process. In order to obtain polymeric materials, with desired properties, by tailoring the benzoxazine monomer with different functionality and a wide variety of monomers can be synthesized by using appropriate chosen phenol and amine. In this section synthesis of different benzoxazine monomers have been discussed.

2.4.1 Mono-functional benzoxazine monomers

Holly and Cope [4] first reported the condensation reaction of primary amines with formaldehyde and substituted phenols for the synthesis of well-defined benzoxazine monomers. According to the reported procedure, this reaction was performed in a solvent in two-steps. Later, Burke found that the benzoxazine ring reacts preferentially with the free ortho positions of a phenolic compound and forms a Mannich bridge [5]. The synthetic procedure of the Mannich condensation for benzoxazine synthesis in a solvent proceeds by first addition of amine to formaldehyde at lower temperatures to form an N,N-dihydroxymethylamine derivative, which then reacts with the labile hydrogen of the hydroxyl group and ortho position of the phenol at the elevated temperature to form the oxazine ring [6] (Figure 2.2).

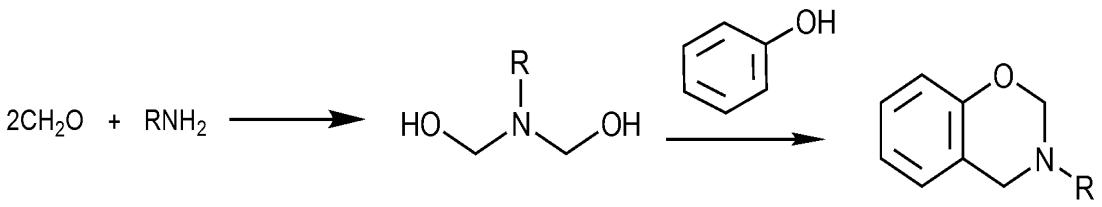


Figure 2.2 Synthesis of 3,4-dihydro-2H-1,3-benzoxazine

As an example, to prepare 3,4-dihydro-3-cyclohexyl-6-*t*-butyl-1,3,2H-benzoxazine, Burke [6] employed two procedures:

(i) Cyclohexylamine was mixed with formaldehyde in dioxane. After addition of *p*-butyl phenol the mixture was refluxed for 2 h. Upon cooling to room temperature, a crystalline product was obtained, which was then recrystallized from 95 % ethanol and the yield was 78 %.

(ii) Paraformaldehyde was dissolved in warm methanolic KOH solution. The solution was cooled during the portion-wise addition of cyclohexylamine. After the addition of 4-*t*-butylphenol, the resulting solution was cooled to room temperature and the product was recrystallized from 95 % ethanol and the yield was 92 %. Synthesis of a *p*-cresol based benzoxazine by using aniline, formaldehyde and *p*-cresol as starting materials in dioxane has been reported [7-9].

It has been observed that for some benzoxazines, the ring opening occurs in the presence of compounds with active hydrogen (HY), such as naphthol, indoles, carbazole, imides, and aliphatic nitro compounds even phenol (which is also one of the starting compound for synthesis) [10] and small oligomers form as by-products. Formation of the Mannich bridge structure due to the ring opening of benzoxazine in acidic medium (HY) [6] is shown below in Figure 2.3

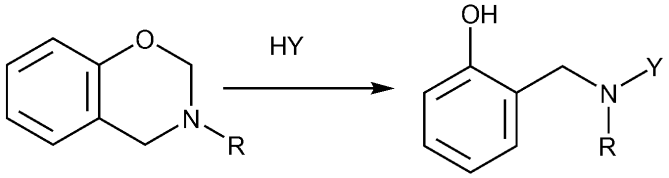


Figure 2.3 Ring Opening of benzoxazine in acidic medium

The slow reaction rate, large amount of solvent required for the synthesis and, in some cases, the poor solubility of the precursors are the major disadvantages

associated with this procedure. The use of an organic solvent also increases the cost of the products and causes environmental problems. Furthermore, the solvent residue in the precursors also leads to problems during processing of the benzoxazine resins. To overcome these shortcomings, solventless synthesis in the melt state was developed [11].

The reaction mechanism and kinetics of this solventless synthesis were proposed [12]. In a typical synthesis, the reactants, *i.e.*, aldehyde, amine and phenolic precursors are physically mixed together, heated to their melting temperature, and thereafter maintained at a temperature sufficient to complete the interaction of the reactants to produce the desired benzoxazine. In this connection, it should be pointed out that formaldehyde is not typically used as it evaporates easily and lose stoichiometry quickly.

Instead, paraformaldehyde is used. The choice for phenols and amines provides the flexibility in designing monomer structure for tailoring the properties of the resulting polybenzoxazine polymer. The main advantages of the solventless synthetic method are improvement of reaction times compared with the traditional synthetic route and formation of fewer unwanted intermediates and byproducts. Although most of the benzoxazines were synthesized by using phenol, formaldehyde and primary amines as starting compounds several other synthetic strategies were also reported. To synthesize 3,4-dihydro-2*H*-1,3-benzoxazine, Firstly [13] *N*-(2- hydroxy-3,5-dimethylbenzyl)-aminopropanoic acid was synthesized via the Mannich reaction between 2,4-dimethylphenol, aqueous formaldehyde, and 3-aminopropanoic acid in ethanol. This amino acid was allowed to react in 96% sulfuric acid at room temperature. After neutralization, 3-(2-hydroxy-3,5-dimethyl)benzyl-3,4-dihydro-6,8-dimethyl-2*H* 1,3-benzoxazine was obtained. The reaction steps are shown in this method, the alkylating agent arises from acid-induced deamination of the phenolic Mannich base.

Thus, the variety of substituent on the N-3 position of the benzoxazine ring is limited. Benzoxazine can also be obtained by heating the mixture of 2,4-xylenol and hexamethylenetetramine (3:4:1 mole) at 135°C for 2 h in air. The reaction of 1 mole of 2-hydroxybenzylamine with 2 moles of formaldehyde produces bis-(3,4-dihydro-2*H*-1,3-benzoxazine-3-yl)-methylene.

Some 3,4-dihydro-2*H*-1,3-benzoxazines with substituents on C-2 or C-4 such as, 2,2-dibenz-1,3-oxazine, were also synthesized, by the reactions of salicylamines(ohydroxybenzylamine) with glyoxal or -diketones in methanol at a temperature lower than 20 °C [14].

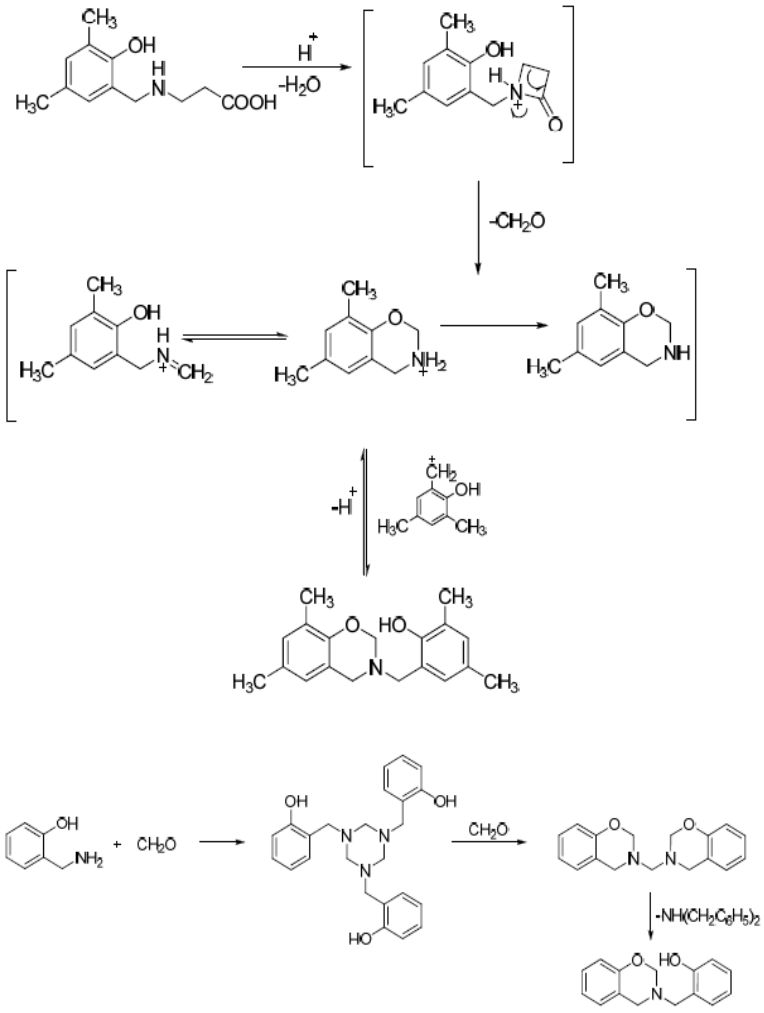


Figure 2.4 Reaction mechanism of synthesis of 3,4-dihydro-2H-1,3- benzoxazine

This offers a predictable and widely applicable synthetic strategy for the regiospecific construction of heterocyclic compounds [15]. 3,4-Dihydro-2*H*-1,3-benzoxazines were synthesized by directed *ortho*-lithiation of phenols and by sidechain lithiation of substituted phenols, respectively, in one-pot by reacting with *N*,*N*bis[(benzotriazol-1-yl)methyl]amines as 1,3-biselectrophile synthons (reaction 2.5)[16].

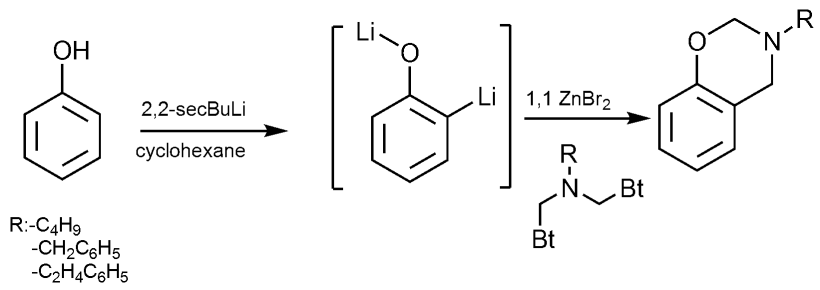


Figure 2.5 Synthesis of 3,4-Dihydro-2H-1,3- benzoxazines by directed ortho-lithiation of phenols

2.4.2 Di-functional and Multifunctional Benzoxazine Monomers

Curing of mono-functional benzoxazines with phenol resulted in the formation of only oligomeric structures with average molecular weight around 1000 Da. Thus, no materials could be made from this approach since the thermal dissociation of the monomer competed with chain propagation reaction so that high molecular weight linear structures were unobtainable [17]. Hemvichian K. *et al.* have reported that the reduction of reactivity is due to the hydrogen bonding formation. Such phenomenon was observed in the temperature range below where reverse Mannich reaction occurs in benzoxazine chemistry [18]. To overcome this limitation, Ishida and coworkers [19, 27] have developed a new class of difunctional or multifunctional benzoxazine monomers, and their curing into phenolic materials with the ring opening reactions being initiated by dimers and higher oligomers in the resin composition.

The main constituent of the resulting products was a monomer with difunctional benzoxazine ring structures at both ends of the bisphenol A. The rest of the composition consisted of a mixture of dimers and oligomers, with both benzoxazine rings and free phenol structures, as detected by NMR, FTIR and SEC. It was observed that, the composition of the products is, to a large extent, dependent on the polarity of the solvent. This synthetic method consists of a few simple steps and can easily provide different phenolic structures with wide design flexibility.

Similar type of difunctional benzoxazine was prepared using aniline instead of methyl amine [28, 29] and the pure monomer was referred as B-a and oligomers were as oligo-B-a. The structures of oligo-B-a and B-a were analyzed by $_1$H-NMR measurements. The overall synthetic procedure is shown in Figure 2.6 [28]. To achieve successful processing, cure kinetics of this material was investigated by using DSC, which indicated that the curing of benzoxazine precursors is an auto-

catalyzed reaction until vitrification is occurred, and diffusion begins to control the curing process afterwards [29].

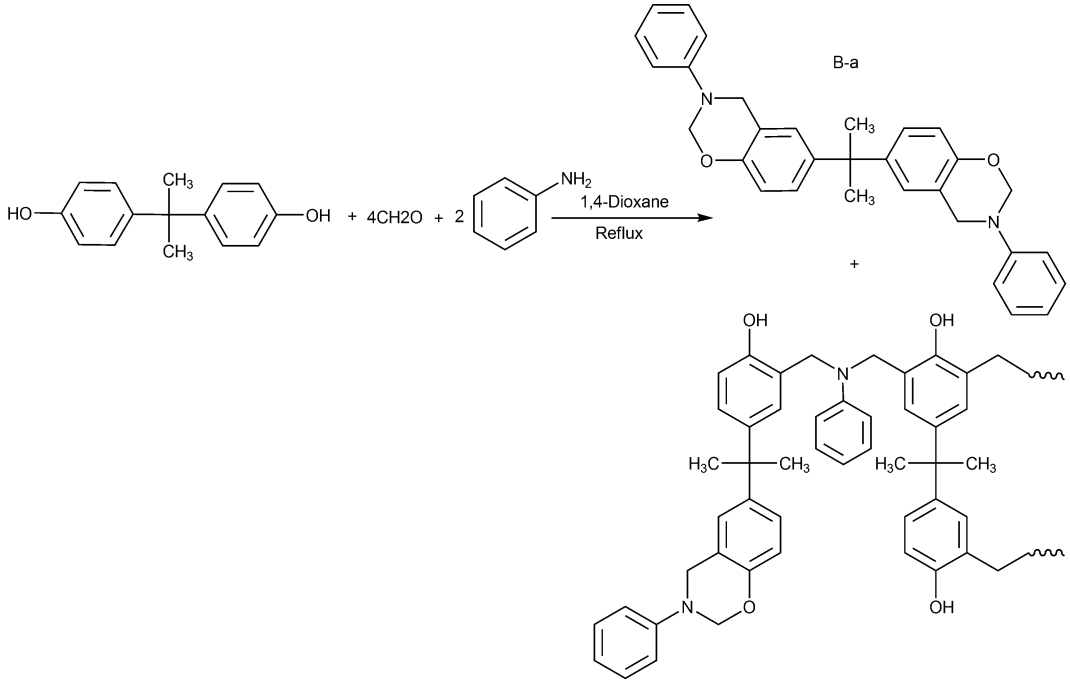
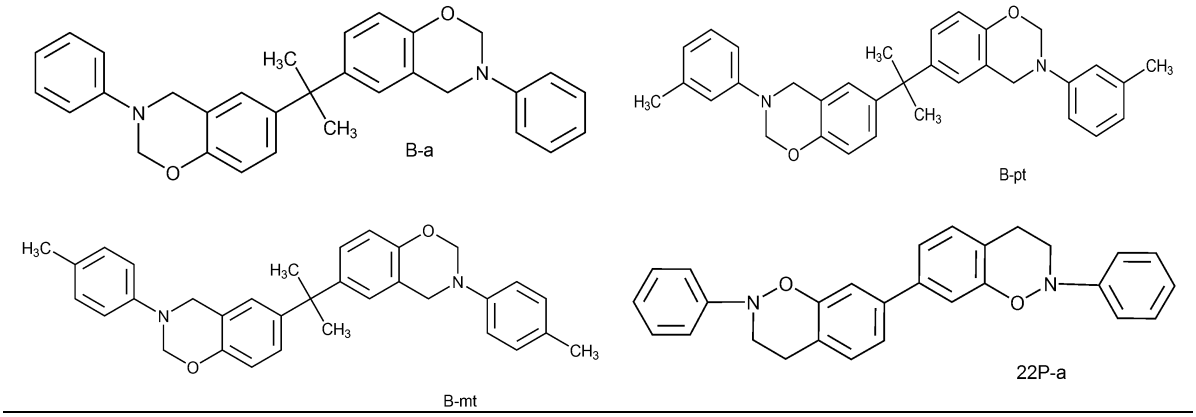


Figure 2.6 Synthesis of bisphenol-A and aniline based benzoxazine (B-a) monomer.

The synthesis Solventless method was successfully employed for synthesis of a series of difunctional monomers listed in table 2.4. [23,28, 30-33]

Table 2.4 Difunctional Benzoxazine Monomers

Benzoxazine Monomers


Reaction Mechanism of Ring Opening Thermal Polymerization of Be to understand the polymerization reaction mechanism of benzoxazines,understanding of the chemical structure of its oxazine ring is very important.

A single crystal X-ray crystallographic study revealed that the preferential conformation of a mono-oxazine ring containing benzoxazine is a distorted semichair structure, with the nitrogen and the carbon between the oxygen and nitrogen on the oxazine ring sitting, respectively, above and below the benzene ring plane. The resulting ring strain from this molecular conformation helps this type of six membered ring to undergo ring-opening reaction under specific conditions. In addition, due to their high basicity (by Lewis definition) both the oxygen and the nitrogen of the oxazine ring can act as potential cationic polymerization initiation site and makes the ring very likely to open via a cationic mechanism [35,36]. The electron charge calculation after energy minimization predicts that oxygen might be the preferred polymerization site over nitrogen due to its high negative charge distribution (O, -0.311; N, -0.270). The ring opening reaction of the benzoxazine was first reported.

In the reaction of 1,3- dihydrobenzoxazine with a phenol, having both *ortho* and *para* position free, it was found that aminoalkylation occurred preferentially at the free *ortho* position to form a Mannich base bridge structure, along with small amount reaction at *para* position. To explain this ortho preferency formation of a intermolecular hydrogenbonded intermediate species was proposed. High reactivity of the *ortho* position was also observed when following the kinetics of mono-functional benzoxazines with 2,4-di-*tert*-butylphenol catalyst. The typical method of polymerization of benzoxazine monomers is thermal curing without using any catalyst [37]. It should be emphasized that the polymerization mechanism of benzoxazine resins is still not well established.

2.5 Thermal polymerization of benzoxazines

A cross-linked network structured polybenzoxazines, with higher Tg and degradation temperature, can be obtained when difunctional or multifunctional benzoxazines undergo polymerization. The polymeric structures form due to curing of mono-functional and difunctional benzoxazines are shown below in Figure 2.12 [38].

Obviously, difunctional benzoxazines derived from diamines are expected to undergo similar cross-linking [39,40].

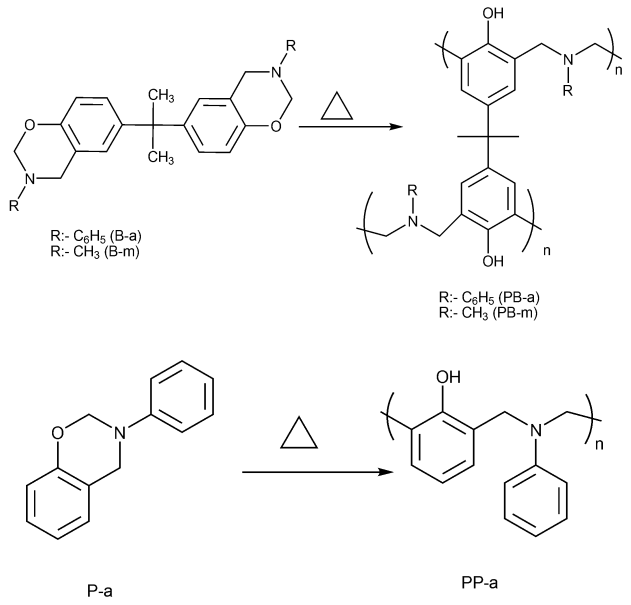


Figure 2. 7 Curing of monofunctional and difunctional benzoxazines

In the DSC thermogram of a mono-functional benzoxazine, P-a, a sharp exotherm was observed with onset and maximum temperatures of the exotherm at 202 °C and 230 °C respectively, corresponding to the ring-opening polymerization. The amount of exotherm for P-a was 62 cal/g. In case of difunctional benzoxazine, B-a, DSC showed an exotherm on with onset at ca. 223 °C and maximum at 249 °C corresponding to the ring-opening polymerization of benzoxazine. The amount of exotherm for B-a was 79 cal/g [39]. It has been observed that during synthesis of a difunctional benzoxazine (from bisphenol A, formaldehyde and methyl amine) not only bisphenol-A based benzoxazine (B-m) monomer forms as major product but also dimers and small oligomers form by the subsequent reactions between the rings and *ortho* position of bisphenol A hydroxyl groups. These free phenolic hydroxy structure containing dimers and oligomers trigger the monomer to be self-initiated towards polymerization and cross-linking reactions [41]. Attempts have been taken to understand the cure mechanism and kinetics of the thermal curing of mono and difunctional benzoxazines utilizing DSC, FTIR, DMA, 13 C and 15 N solid sate NMR spectroscopic measurements [42,43-49].

It has been proposed that, the ring-opening initiation of benzoxazine results the formation of a carbocation and an iminium ion which exist in equilibrium [43] (Figure 2.11). Polymerization proceeds via the electrophilic substitution by the carbocation to the benzene ring. This transfer occurs preferentially at the free ortho and para position of the phenol group**.** The stability of the iminium ion greatly affects the propagation rate because carbocation is responsible for propagation. Further, the reactivity of the equilibrium pair depends on the basicity of the amine group. The more basic the amine, with more the free electron density of the nitrogen, has the capability to stabilize more the positive charge of the iminium ion. If the iminium ion is more stable, the equilibrium shifts toward it, causing lowering in propagation rate. If the iminium ion is unstable, the equilibrium will be shifted toward the carbocation, resulting in a higher propagation rate.

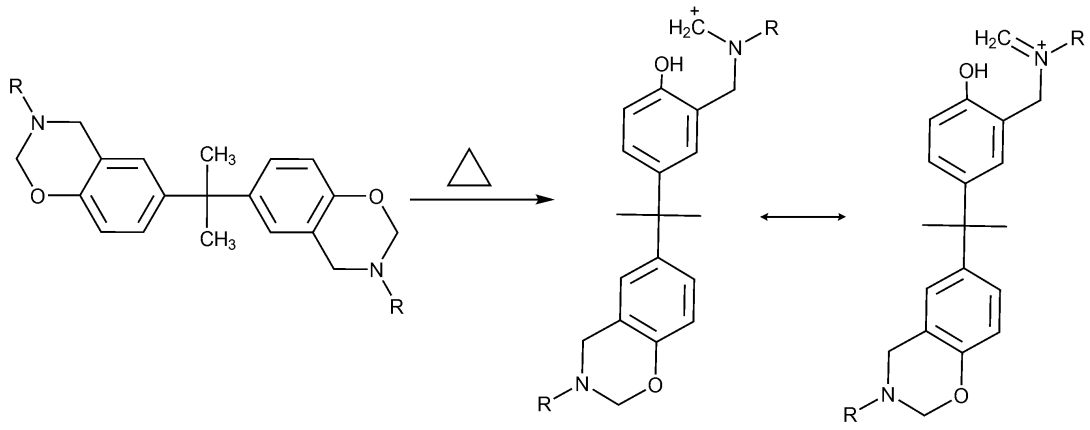


Figure 2.8 Initiation of ring-opening polymerization of benzoxazine

It should be noted that since the propagation reaction involves chain transfer to a benzene ring temperature should have a great impact on the rate of propagation. Kinetic study indicated that in the early stages of polymerization, the reaction may be relatively independent of the cure temperature. As the reaction proceeds, the temperature effect on propagation becomes more evident in the reaction kinetics.

Curing reactions at two different temperatures, below and above Tg temperature, demonstrate that the kinetics are significantly different for the two cure temperatures. Vitrification occurs sooner at higher cure temperature than the lower cure temperature, especially below the Tg. As vitrification causes a large increase in the viscosity of the system, at the reaction becomes largely diffusion-controlled, and

greatly affect the curing kinetics [43]. Figure 2.12 illustrates the thermal polymerization of B-a through cationic mechanism.

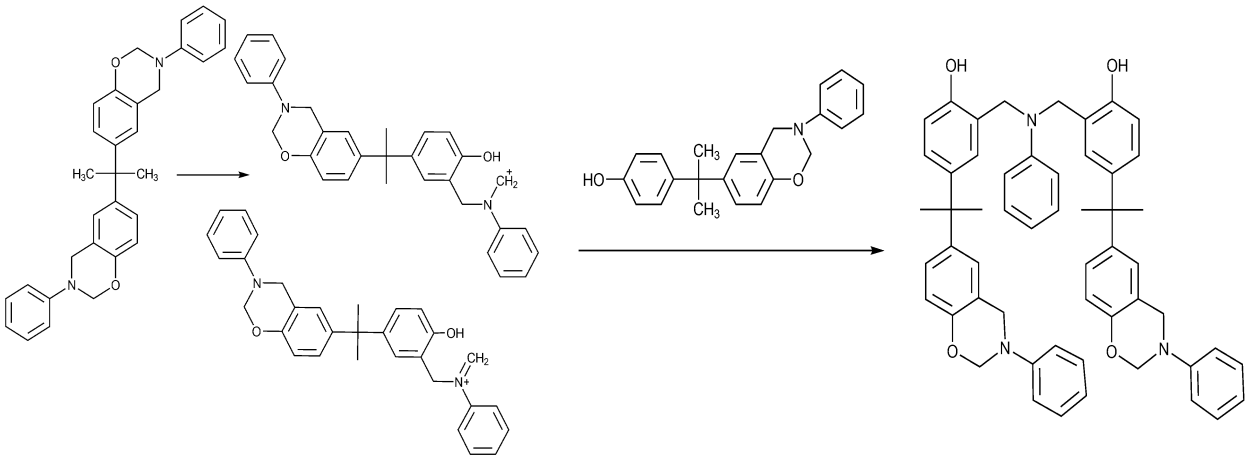


Figure 2.9 Thermal polymerization of B-a through cationic mechanism

Invention compositions are especially useful for increasing adhesion at interfaces. Optionally, the composition can also include a curing agent and/or filler. These compositions are mainly used as adhesives, encapsulants and coatings. Within the semiconductor fabrication industry, materials such as die attach adhesives, films, underfill materials and lead free solders are developed. PBZ compositions have near-zero volume change after post cure and this enables the usage of them as coating material. Heat curable composition of benzoxazine is useful in aerospace industry applications. Thermosetting benzoxazine resin compositions can bind a substrate to a metallic surface [60,61]

2.6 Flame Retardancy

The need to protect materials against fire has been a scientific udertaking for a very long time.The earliest fire retardants for synthetic polymers were halogen based, based on the discovery of the halogenated hydrocarbons. The flammability characteristics of benzoxazine is very similar to the phenolic resin due to the formation of very similar net work created after polymerization. Benzoxazines is a candidate of choice for industries interested to replace phenolic resins because of toxicological issues in the workshops before or upon curing along with very good fire retardant properties. The basic chemical repeat unit contains a phenolic and

tertially amine units both of which have been considered the chemical group for good anti-flammability characteristics. Benzoxazine polymers employing halogen-free approaches is an attractive topic, since these polymers are applied in electronic products which would form highly crosslinking network structures after cure. Thus, the glass transition temperature and the thermal decomposition temperature of polybenzoxazines would be improved significantly in comparison with typical polybenzoxazines.

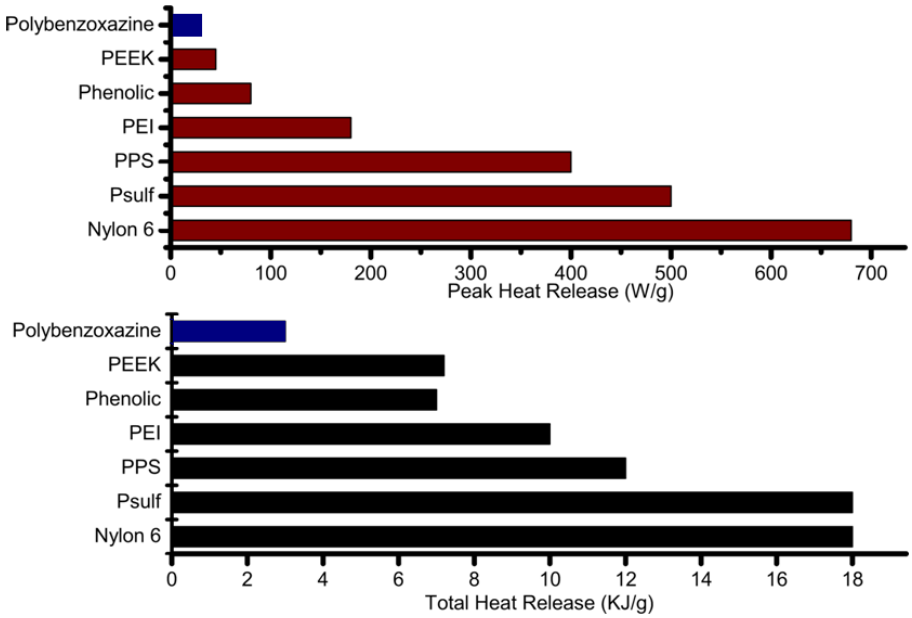


Figure 2.10 Flammability of high performance polymers

2.7 Methodology of Synthesis Imide Containing Polybenzoxazines

Polyimides are considered as high performance polymers containing imide moieties in the molecular backbone. They have unique temperature stability, high mechanical performance and excellent chemical resistance. Thermoset polyimides exhibit very low creep and high tensile strength. These properties are maintained during continuous use to temperatures of 232 °C and for short excursions, as high as 482 °C. Polyimides are also inherently resistant to flame combustion and do not usually need to be mixed with flame retardants. They have improved thermal and thermo-oxidative resistance, chemical resistance, and high mechanical strength; they face

numerous processibility issues due to their high viscosity and low solubility in organic solvents.

For Benzoxazine monomers with imide functionalities, showed improved thermal properties. The DSC and FT-IR studies of maleimide containing monomer, HPM-Ba, revealed that polymerizations occurs in two stages in the temperature range from 120 to 250°C (i) polymerization of C=C bonds of maleimide group at about 150°C by free radical mechanism, and (ii) the ring opening polymerization of oxazine at about 230°C. DSC thermograms of MIB showed benzoxazine polymerization occurred at 213 and 261°C, respectively. The char yields and T_g of the benzoxazine based polymers has also been increased due to incorporation of these additional functionalities, since they improve the network structure by providing extra cross-linking.

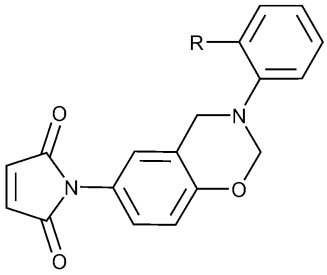


Figure 2.11 Maleimidyl functional benzoxazines

3. EXPERIMENTAL PART

3.1 Materials

Benzylamine (Merck, 99%), paraformaldehyde (Aros, 96%), sodium hydroxide (Acros, 97%), methanol (Aldrich, ≥99%), diethylether, 1,4-dioxane (Aldrich, ≥99%), chloroform (Acros, 99+%), toluene (Aldrich, 99%), phtalic anhydride

(Merck, 98%), tetrabromo phtalic anhyride (Aldrich, 98%), hexachloronorbornene phtalic anhydride (Acros, 96%), 4-aminophenol (Merck, 99%), DMF

(Merck,99%), para-xylene (Fluka, 98%), hexane (Carlo Erba, 95%), THF (Carlo Erba, 98%) were used as received.

3.2 Objectives Characterization

3.2.1 Nuclear magnetic resonance spectroscopy (NMR)

^{1}H-NMR measurements were recorded in $CDCl_3$ with $Si(CH_3)_4$ as internal standard, using a Bruker AC250 (250.133 MHz) instrument.

3.2.2 Infrared spectrophotometer (FT-IR)

Differential scanning calorimeter was performed on a Perkin Elmer Diamond DSC with a heating rate of 10°C min^{-1} under nitrogen flow.

3.2.3 Thermal gravimetric analysis (TGA)

TGA was carried out on Perkin Elmer Diamond TA/TGA with a heating rate of 10°C min^{-1} under nitrogen flow.

3.3 Preparation methods

3.3.1 Preparation of 1, 3, 5-tribenzyl-1, 3, 5-triazinane

1,3,5-tribenzyl-1,3,5-triazinane was synthesized by mixing stoichiometric amounts of paraformaldehyde (0.018 mol, 0.56g), benzylamine (0.018 mol, 2 g) for 2 hours at

100 °C with addition of 75 ml toluene under continuous stirring. After evaporation of toluene,the product was dissolved in chloroform and washed with a 0.2 N sodium hydroxide and recrysallized from diethylether.White cystals were obtained.

3.3.2 Preparation of imide derivatives

Preparation of Phtalimide, tetrabromo Phtalimide and hexachloro-5-norbornene-imide:

The general procedure is as follows; The phtalic anhydride (0.037 mole, 5g), tetrabromo phtalic anhydride (0.011 mole, 5g) and hexachloronorbornene phtalic anhydride (0.013 mole, 5g) was dissolved in 50 ml DMF respectively. 4-aminophenol (0,037mole, 4.03g) in 20 ml DMF was gradually added. The solution was stirred for 1,5 hours in an ice bath, followed by imidization Dean-Stark instrument was used and stirred for 24 hours at 130 °C.After vacuum drying solid powder was obtained.

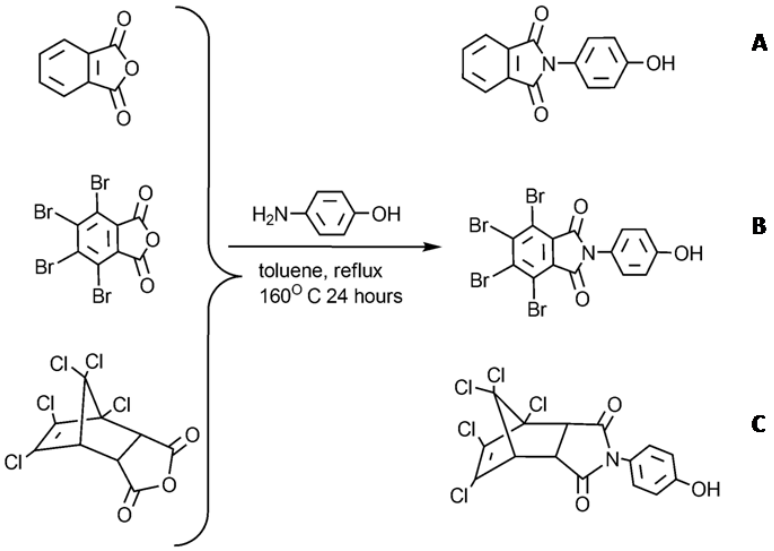


Figure 3.1 Preparation of (A) Phtalimide, (B) Tetrabromo Phtalimide and (C) Hexachloro-5-norbornene-imide

3.3.3 Preparation of monofunctional benzoxazine monomer

Preparation of Phtalimide Containing Benzoxazine , Tetrabromo Phtalimide Containing Benzoxazine ,Hexachloro-5-norbornene-imide containig Benzoxazine :

Phtalimide, TetrabromoPhtalimide, Hexachloro-5-norbornene-imide(4 mmole,0,5g) were mixed with m1 (14 mmole, 0.25g) and paraformaldehyde (4 mmol, 0063g) and reacted at 130 °C for 1,5 hours respectively. 100 ml para-xylene was added into the reaction mixture. The solution was cooled to room temparature and poured into hexane to obtain yellow powder. The powder was redissolved in THF and reprecipitated in methanol. Brown crystals were obtained.

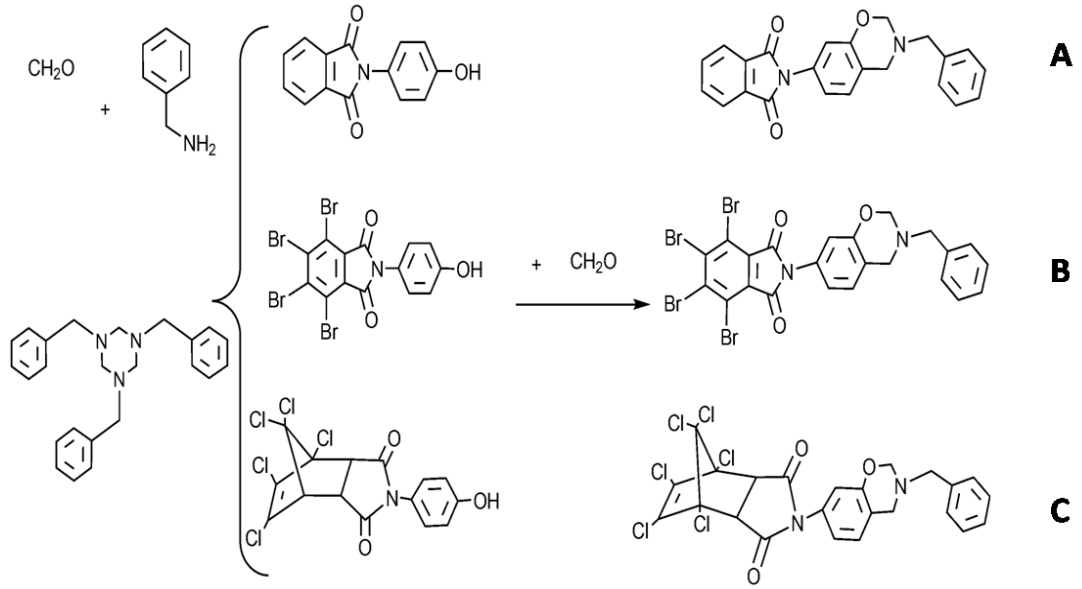
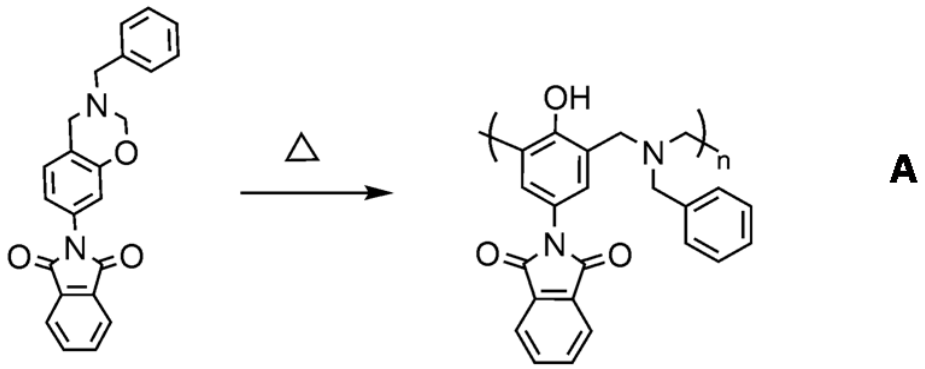


Figure 3.2 Preparation of (A) phtalimide benzoxazine, (B) tetrabromo phtalimide benzoxazine, (C) hexachloro-5-norbornene-imide benzoxazine

3.3.4 Polymer synthesis



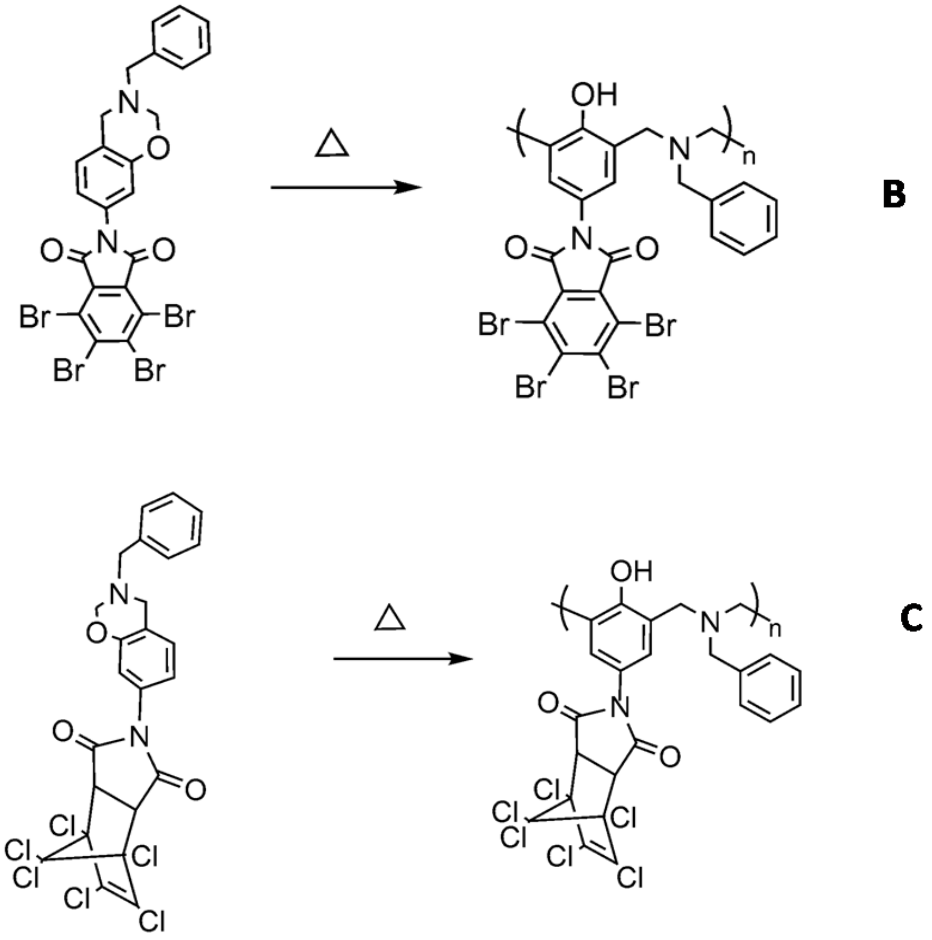


Figure 3.3 Preparation of (A) Phtalimide polybenzoxazine, (B) Tetrabromo phtalimide polybenzoxazine, (C) Hexachloro-5-norbornene-imide polybenzoxazine

4. RESULTS AND DISCUSSIONS

Thermally curable monofunctional polybenzoxazine with imide derivatives is synthesized by the imidization reaction after followed by ring-opening reaction. First imide functional groups synthesized by the imidization reaction. Secondly imide containing benzoxazine is formed as a monomer with solventless method. Finally the desired thermally curable and flame retardant product was yielded. The details of procedure will be given below.

4.1 Synthesis and Characterization of 1, 3, 5-tribenzyl - 1, 3, 5-triazinane

Condensation of primary amines with formaldehyde and substituted phenols yields well-defined benzoxazine monomers. Traditionally, this reaction was performed in a solvent as a two-step synthesis according to the procedure first described by Holly and Cope [62]. Later, Burke found that the benzoxazine ring reacts preferentially with the free *ortho* positions of a phenolic compound and forms a Mannich bridge[63]. The reaction mechanism of the Mannich condensation of the benzoxazine synthesis in a solvent proceeds by first adding amine to formaldehyde at lower temperatures to form an *N*,*N*-dihydroxymethylamine, which then reacts with the labile hydrogen of the hydroxyl group and *ortho* position of the phenol at the elevated temperature to form the oxazine ring[64]. The slow reaction rate, large amount of solvent required for the synthesis and, in some cases, the poor

solubility of the precursors are the disadvantages of this procedure.

The use of an organic solvent also increases the cost of the products and creates the environmental problems of disposal. Furthermore, the solvent residue in the precursors leads to problems during processing of the benzoxazine resins. To overcome these shortcomings, a solventless synthesis in the melt state[4]was developed. The reaction mechanism and kinetics of the solventless synthesis were proposed by Liu and Ishida in order to use this procedure to prepare a large quantity of benzoxazine monomers[65].

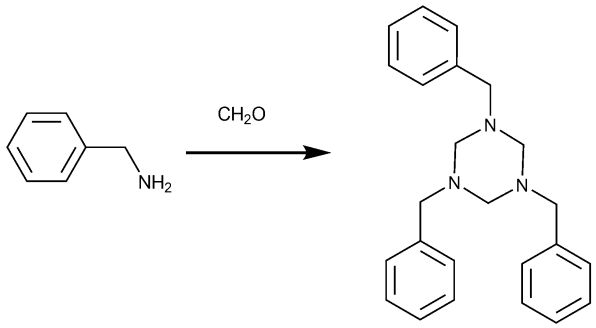


Figure 4. 1 Preparation of triazinane derivative

The chemical structure of triazinane structure was confirmed by both FT-IR and ^{1}H-NMR spectroscopy. FT-IR spectrum presented in Figure 4.2 (a) shows characteristic absorptions of tirazinane structure at 1559 cm^{-1}, 1499 cm^{-1} and 755 and 692 cm^{-1} (monosubstituted benzene ring), absorption bands of 1163, 1203 and 1336 cm^{-1} group are (C-N-C). There is no evidence of the presence of the amine functionalities, since there is no band at 3200–3250 cm–1, which is usually assigned to the NH stretching. The C-H out-of-plane vibration of the benzene ring is found at 936 cm^{-1} in this spectrum.

The ^{1}H-NMR spectrum shown in Figure 4.3 also establishes the structure of 1, 3, 5-tribenzyl - 1, 3, 5-triazinane. The resonance at 3.68 ppm is suggested to come from the methylene units. The resonance at 7.25 ppm is assigned on the protons of the benzene group.

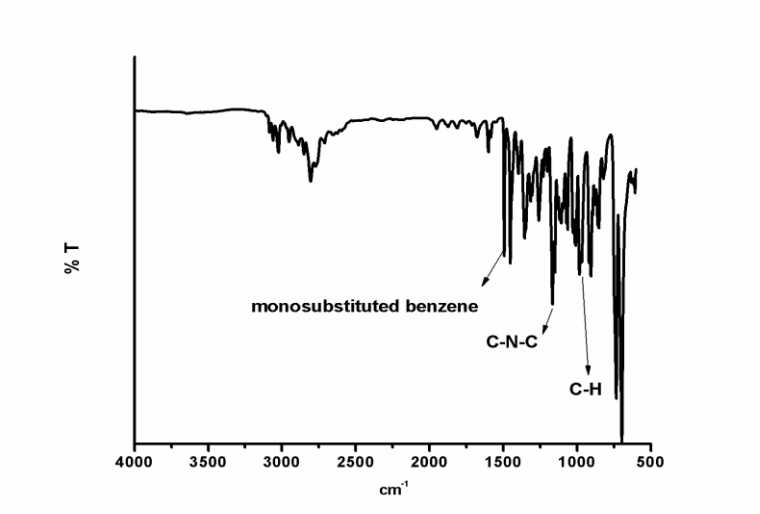


Figure 4.2 FT-IR Spectrum of triazinane derivative

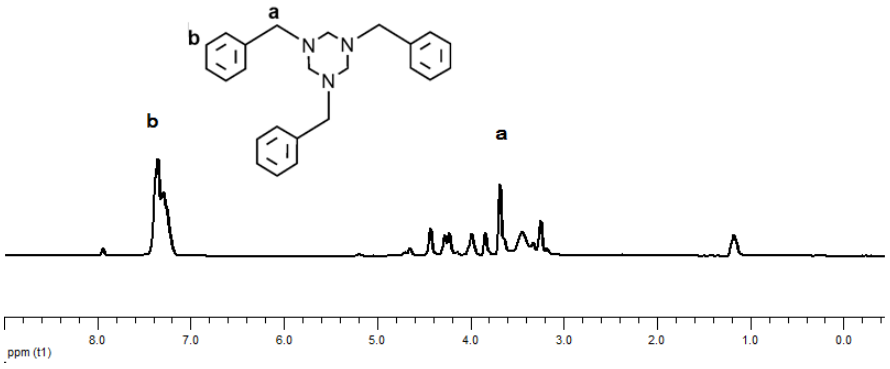


Figure 4.3 NMR Spectrum of triazinane derivative

4.2 Synthesis and Characterization of Imide derivatives

In this study, imide derivatives was selected as semi-product for synthesizing monomers of benzoxazine, which was prepared according to the modified procedure described by Agag and Takeichi [66]41.

The chemical structure of imides was confirmed by both FT-IR and ^{1}H-NMR. FT-IR spectrum presented in Figure 4.4 shows characteristic absorptions of imide structure at 1700 cm^{-1},1210 cm^{-1} (C-O), absorption band of 3400 cm^{-1} group are

(-OH). ^{1}H-NMR spectrum of imide structures with gave further support to its chemical structure (Fig. 4.5). The aromatic C-OH was characterized with the absorption peaks 9.56, 7.23ppm(-C(=O)N and at 6.93 (-NC(=O) .

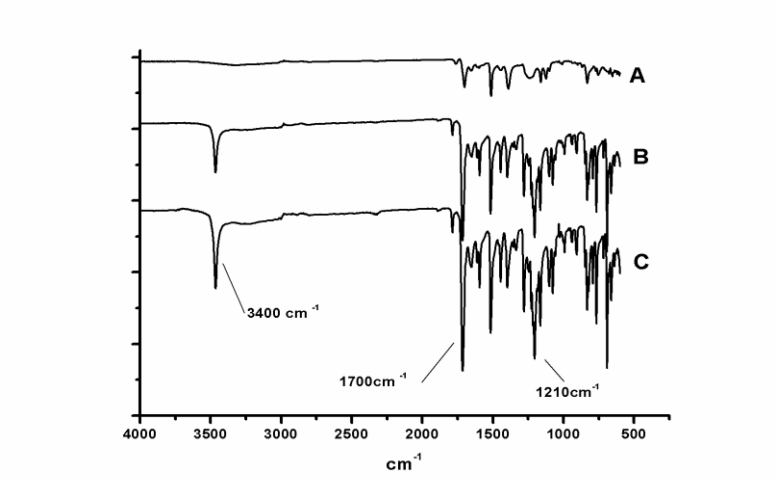


Figure 4.4 FT-IR Spectrum of (A) Phtalimide, (B) Tetrabromo phtalimide, (C) Hexachloro-5-norbornene-imide

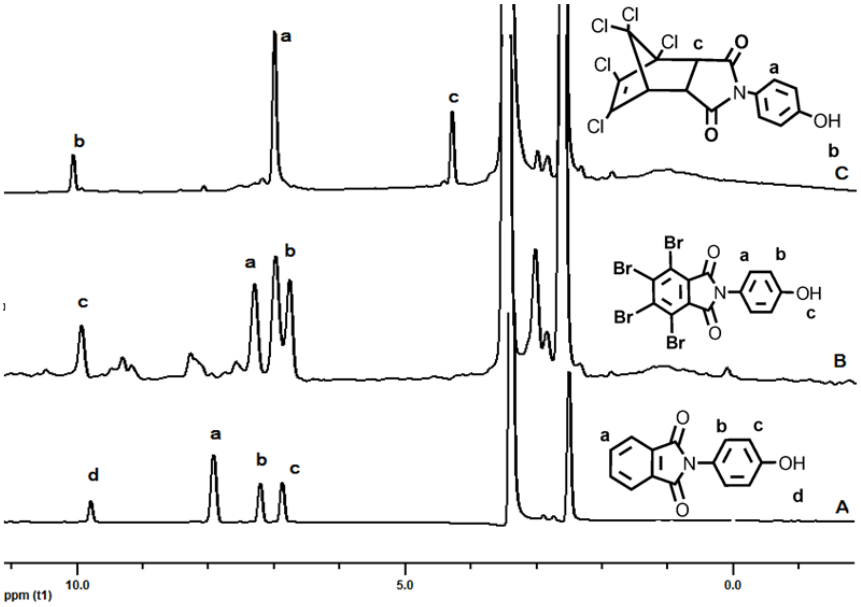


Figure 4.5 NMR Spectrum of (A) Phtalimide, (B) Tetrabromo phtalimide, (C) Hexachloro-5-norbornene-imide

4.3 Synthesis and Characterization of monofunctional benzoxazine monomer

Synthesis and characterization of Phtalimide benzoxazine, Tetrabromo phtalimide benzoxazine , Hexachloro-5-norbornene-imide benzoxazine:

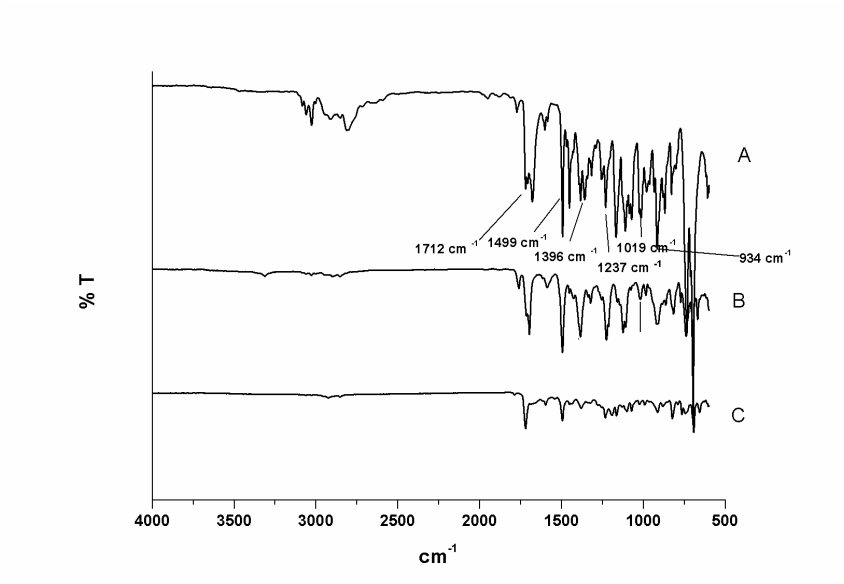


Figure 4.6 FT-IR Spectrum of (A) Phtalimide benzoxazine, (B) Tetrabromo phtalimide benzoxazine, (C) Hexachloro-5-norbornene-imide benzoxazine

FT-IR spectrum (Fig 2.19) at 1237 cm^{-1} (asymmetric stretching of C-O-C), at 1029 cm^{-1} (symmetric stretching of C-O-C), at 1396 cm^{-1} (-C-N-), and at 934 and 1499 cm^{-1} (trisubstituted benzene ring).[67-38] Absorption bands in the FT-IR spectrum at 691 cm^{-1} (C - C), at 1150 (stretching of C-N-C), at 1594 cm^{-1} (stretching of C - C), and at 1712 cm^{-1} (stretching of C -O) were assigned to the imide group.

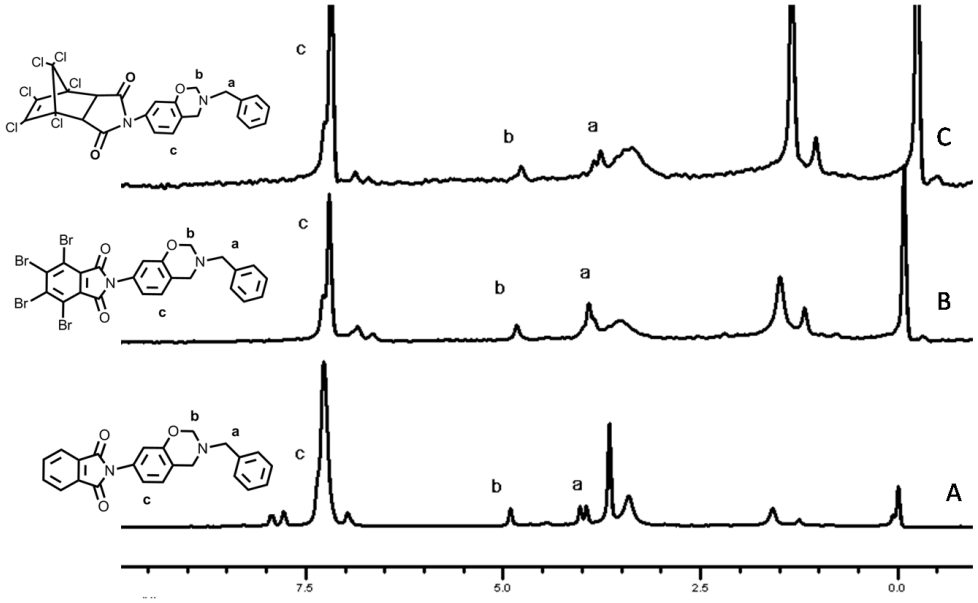


Figure 4.7 NMR Spectrum of (A) phtalimide benzoxazine, (B) tetrabromo phtalimide benzoxazine, (C) hexachloro-5-norbornene-imide benzoxazine

^{1}H-NMR spectrum of benzoxazine structures with imide funcionality gave further support to its chemical structure. The oxazine ring was characterized with the absorption peaks at 4.231 (-Ph- CH_2-N-) , 5.06 ppm

(-O-CH_2-N-)[69,70] and at 7.25 (-Ar-). The imide group was characterized with the absorption at 6.89 ppm (-CH-CH-) .[71,72] On the other hand, no absorption peaks at 3.0 to 4.0 ppm were observed in the ^{1}H-NMR spectrum, to indicate that there were not ring-opened by products left in the product.[69,70]

4.3.1 Thermally Activated Curing of monofunctional benzoxazine monomer

As a high performance thermoset, polybenzoxazines have thermal stability with high char yield. In our case, incorporation of benzoxazines with halogen containing imides should provide this desired property which is high thermal stability. A main weight loss around 400°C which is assigned overall amine evaporation that is the

consequence of the Mannich base cleavage of the polybenzoxazine. Weight losses after 400°C can be attributed to the imides with free halogens decomposition and following thermal aromatization and crosslinking during degradation which finally leads to char formation. Besides, it exhibits comparable char yield and 5%, 10% weight losses to many polybenzoxazines. 10% weight loss temperatures (*T5* and *T10*) for cured phtalimide, cured tetrabromo phtalimide and cured hexachloro-5-norbornene-imide were determined at 227, 271 and 308 °C. The char yield of phtalimide was 15% at 800 °C. The char yield of cured hexachloro-5-norbornene-imide (34%) increased of much more than that cured tetrabromo phtalimide (26%) mainly because of the nature of the effects of the free halogens on the imide functional groups. The comparative TGA is illustrated in Figure 4.8 and the results are summarized in Table 4.1.

Table 4.1 Thermal properties of the cured phtalimide , cured tetrabromo phtalimide, cured hexachloro-5-norbornene-imide

Polymer c (%)	$T_{5\%}$(°C)	$T_{10\%}$ (°C)	T_{max} (°C)	Y_C (%)
Cured phtalimide	201	227	340	15
Cured tetrabromo Phtalimide	256	271	376	26
Cured hexachloro -5-norbornene-imide	296	308	439	34

$T_{5\%}$: The temperature for which the weight loss is 5%
$T_{10\%}$: The temperature for which the weight loss is 10%
Y_c : Char yields at 800°C under nitrogen atmospher

The thermally activated cure behavior of polymer was studied by differential scanning calorimetry (DSC). Cured phtalimidebenzoxazine showed an exotherm（Figure 4.31）with onset at 210°C and a maximum at 218 °C corresponding to the ring-opening polymerization of benzoxazine. Cured tetrabromo phtalimide benzoxazine showed an exotherm starting at 216 °C with the maximum point at 248 °C and was also much higher than that of cured phtalimidebenzoxazine. For the system of cured hexachloro-5-norbornene-imide benzoxazine, the results in showed that the exothermic peak was observed with the onset at 250 °C and maximum point at 310 °C which was much higher than the others. It is because that

the halogens on the functional group of imide which shows thermally stable character.

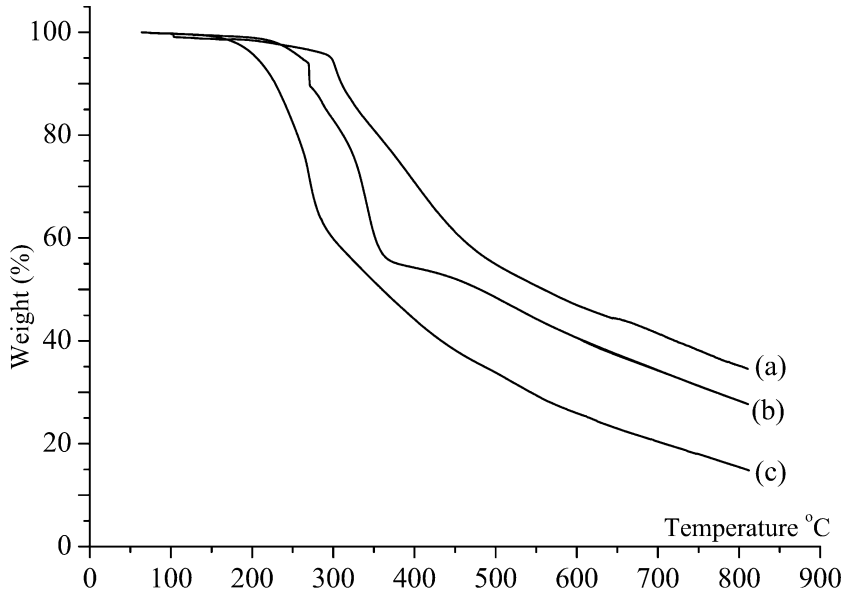


Figure 4.8 TGA thermograms of (a) cured phtalimide benzoxazine , (b) cured tetrabromo phtalimide benzoxazine, (c) cured hexachloro-5-norbornene-imide benzoxazine

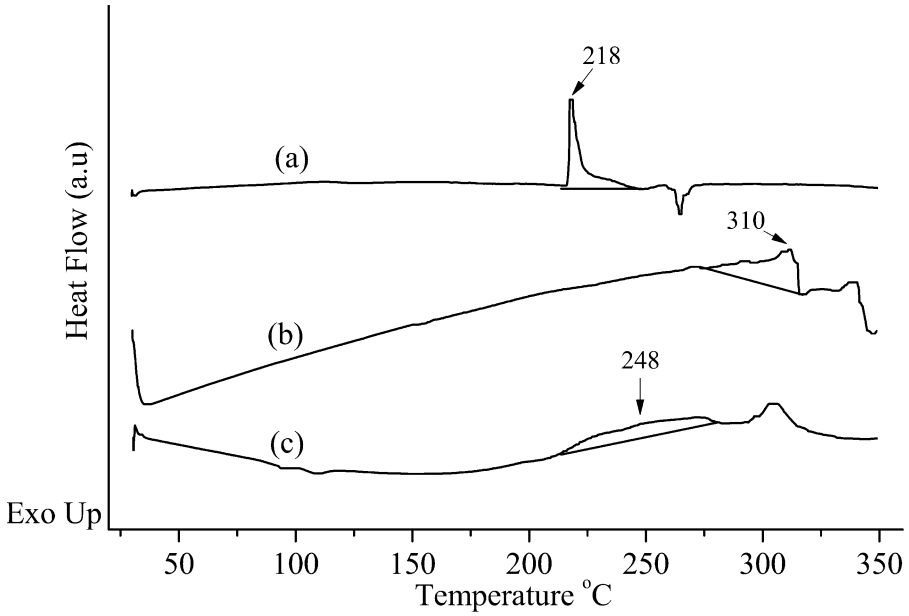


Figure 4.9 DSC data of (a) cured phtalimide benzoxazine , (b) cured hexachloro-5-norbornene-imide benzoxazine, (c) cured tetrabromo phtalimide benzoxazine

5. CONCLUSION

In conclusion, we have synthesized high thermally stable imide containing polybenzoxazines. The enhanced thermal stability was attributed to presence of the imides with halogens. These features give an opportunity to form non-flammable and thermally stable polybenzoxazines. The curing process requires no additives and polymers are simply heated to give cross-linked networks. Further studies in this line are now in progress.

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